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DELAWARE UNIV NEWARK DEPT OF CHEMICAL ENGINEERING F/G 13/8
DEVELOPMENT OF SUPERIOR DENITROGENATION AND ISOMERIZATION CATAL--ETC(U)
NOV 81 J R KATZER, H KWART, A B STILES N00019-80-K-0507

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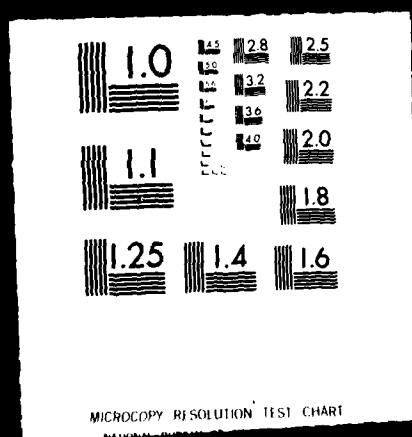
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DEVELOPMENT OF SUPERIOR DENITROGENATION AND
ISOMERIZATION CATALYSTS FOR PROCESSING CRUDE OIL
DERIVED FROM SHALE. PART II

Final Report on Project N00019-80-K-0507
for Naval Air Systems Command

Interim Report on Total Project.
This report covers the period up to November 1, 1981
when funds were exhausted for Part II funding.
Funding for Part III had not been received.

by

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

Principal Investigators:

James R. Katzer (Now with Mobil Oil Corp.)
Harold Kwart
Alvin B. Stiles

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Preface

This work has been a part of a complete detailed study of hydrodenitrogenation and hydrodesulfurization of the more refractory heterocyclic nitrogen and sulfur-containing compounds. One phase of the study involved a diagnosis of the mechanism and routes for S and N to be removed from these heterocyclic compounds. This information was presented in the eleventh quarterly and final reports of the work to DOE. These were supplied to NASC.

This work is to be continued for DOE as an applied study related to crude from coal and heavy petroleum crudes. An initial project was submitted but was rejected for the reason that funds from DOE were not currently available. It is to be submitted by February 15, 1982, to DOE in response to their request for projects relating to coal processing.

The already completed two parts of this project which was funded by NASC has revealed much that is promising in applying our efforts to derive new catalysts especially designed for processing the shale-derived crude as well as the other crudes from heavy petroleum and coal. Subsequently, this will be discussed more completely herein, but presently the pressing need is for renewed funding as requested in our Part III of the project transmitted to NASC early in August 1981.

Introduction and Abstract

A number of facts have been observed during the course of the study and these have led to further tests or catalyst preparations, some of which have been completed, but many are in obeyance awaiting funding. The observations and facts are as follows.

1. The support is an extremely critical factor influencing the catalyst performance profoundly. Not only is the composition of the support critical but the method of preparation is equally critical. This makes for a complex test network to optimize the support, particularly since the best candidate we presently have is a three-component oxide system.

2. The hydrogenation characteristics of the catalyst are critical, and the ratio of MoO_3 to hydrogenation metal also seems to be influenced by the support (possibly acidity or reactivity to form a solid-state reaction product between the composite support and the hydrogenation metal).

3. The sulfiding of the catalyst prior to and during use is influenced by the support composition and hydrogenation metal. New presulfiding techniques probably will be required. It was observed in our desulfurization test with one of these unique compositions that the rate of denitrogenation increased about 20% midway through the tests. This is interpreted as a sulfiding effect, and work is planned to

elucidate this observation; it can be a major discovery of factors influencing catalyst performance.

4. HDN rates as high as three times that of a standard commercial catalyst (3.5% Ni, 18% MoO_3 , 78% gamma alumina) was achieved for alaphatic amines, but this was not followed by similar improvement in shale oil. This observation is unquestionably important, and it must be resolved.

5. Presently more than ten catalysts have been made to pursue the above observations, and more than 20 tests have been designed but cannot be consummated until funding is forthcoming.

Literature Pertinent to the Study

There is attached a tabulation of the pertinent patent and open literature that we have uncovered that relates to the study. One important new reference is listed, "Improved Routes for Making Jet Fuels from Shale Oil," Chemical Engineering, December 28, 1981, pp. 39-41. In this reference the flow sheets and operating characteristics of the process proposed by UOP, Suntech, Ashland Petroleum Co., and Amoco are briefly described. The Amoco process is the only one (like our objective) which uses a single catalyst to achieve the denitrogenation. This catalyst comprises 1.5% CoO , 10% Cr_2O_3 , 15% MoO_3 on a support composed 50% gamma alumina and 50% molecular sieves (H form of γ type). We have examined

a catalyst of the presumed type, and in our tests found it to be less active than our catalyst of highest activity. Our data do not include life tests, so that may be a factor, although we know of no disclosure of Amoco's catalyst life.

Catalyst Preparation, Evaluation and Analytical Facilities

The catalyst preparation is simple precipitation and impregnation equipment fabricated from glass or ceramic to minimize contamination from the equipment itself. Drying, calcining, and sulfiding are isolated facilities not used for other catalysts or chemical salts.

The test facility is a 300 ml autoclave capable of operating at 250 psi and up to 450°C at this pressure. There are ports in this agitated autoclave permitting the introduction of the reactants and catalyst as a slurry and the periodic pressuring with H_2 as required to restore the pressure to the desired level while hydrogen is absorbed in the reaction. Samples of the reactant slurry also can be withdrawn as needed for analytical purposes.

The overall scheme of catalyst preparation, testing, and analysis has been reliable and reproducible. It gives us confidence in the dependability of the results.

Test results and untested catalysts are all tabulated in the attached Tables Nos. 1, 2 and 3 as to composition, test conditions, and results expressed as K value. The higher the K value, the more active the catalyst.

Summary of Results

A variety of supports has been prepared and has also been impregnated with catalytic material comprising Co, Mo, or Ni and Mo. The supports have shown a wide difference in performance with the Al_2O_3 - TiO_2 - Cr_2O_3 showing exceptional promise.

The catalyst has been made with Co and with Ni for the denitrogenation of shale oil; the Ni-Mo catalyst appears to be better than Co-Mo. It also appears that higher concentrations of Ni (3.5% vs. 1.5%) produce a better catalyst.

The Ni-Mo catalyst supported on Al_2O_3 - TiO_2 - Cr_2O_3 was surprisingly active for the HDN of an alkyl amine, decyl amine. In comparison with commercial catalyst, this exploratory catalyst was more than three times as active. Other modified supports were also more active than commercial, but not as active as that supported on Al_2O_3 - TiO_2 - Cr_2O_3 .

The Al_2O_3 - TiO_2 - Cr_2O_3 catalyst did not attain this differential when used on a heterocyclic aromatic compound. The evidence from other tests is that the Ni-Mo moiety is unsufficiently active for the hydrogenation requirement and this must be enhanced.

A second factor is that the more acidic support Al_2O_3 - TiO_2 - Cr_2O_3 retards sulfiding of the catalyst, and the presulfiding should be performed at a lower temperature or

higher partial pressure of H_2S . This observation resulted from a marked increase in HDN midway through a test interpreted to mean that optimum sulfiding had occurred midway through the HDN test.

The HDN of shale oil appears to differ from our experience with either aromatic or paraffinic model compounds. Most tests in the future will be conducted on shale oil.

Evidence is that tests should be run at both higher temperature and pressure. This also will be a future policy.

Program

The program is implied in the abstract section and is evident from the foregoing notations on the above data. However, a further brief summary of the program is as follows.

1. The single most prominent observation is the profound effect on the catalyst of the support. The most effective support was a coprecipitated alumina-chromia-titania composite. The source of the alumina and chromia was the nitrate, whereas the titania was derived from the hydrolysis of an ester of titania. The ratio of these ingredients should be optimized and the titania should be derived from other sources such as titanium sulfate. Additionally, zirconia, rare earths, ZSM-5 molecular sieves, tellurium modified molecular sieves, vanadia, niobia, and tantalum should be studied briefly to determine effect for possibly a more

thorough study. These have been selected because of their likelihood to develop unique surface and pore characteristics.

2. The chemical composition of the catalyst will be studied with the emphasis being directed to increasing hydrogenation rate and ammonia desorption. Factors affecting these results are the addition of promoter quantities of rhenium, ruthenium, iridium, rare earths, and magnesium. The latter could be a component aimed at forming a spinel or perovskite for specific geometric effect.

3. The sulfiding conditions for the final chemical and physical composition must be optimized as to temperature and pressure. The sulfiding agents also could be briefly considered [H_2S , CoS , CS_2 , $(\text{Me})_2\text{S}$].

4. The pore distribution and pore control methods for the support and finished catalyst should be considered.

5. Pretreatment of the crude shale oil should be examined for demetallization and arsenic removal.

Funds Expended to Date

All funds have been exhausted, and accounting of the budgeted and actual expenditures is summarized for both parts on the next page.

NASC Shale Crude - Phase I

<u>Category</u>	<u>Awarded</u>	<u>Expended Encumbered</u>
Co-Investigators		
Katzner	965	965
Kwart	1,119	1,119
Stiles	1,169	1,170
Postdoctoral Associate	8,000	4,061
Graduate Student	0	7,435
Clerical	800	908
Fringe Benefits	1,194	1,094
Supplies & Expense	3,300	3,490
Travel	600	116
<u>Equipment</u>	<u>5,500</u>	<u>-</u>
Total Direct Costs	22,647	20,358
<u>Total Indirect Costs</u>	<u>6,516</u>	<u>7,737</u>
Project Totals	29,163	28,095
Balance		<u>1,068</u>

NASC Shale Crude - Phase II

<u>Category</u>	<u>Awarded</u>	<u>Expended Encumbered</u>
Co-Investigators		
Katzner	965	0
Kwart	1,119	1,119
Stiles	1,460	4,714
Postdoctoral Associate	8,000	8,875
Graduate Student	4,000	3,664
Fringe Benefits	1,196	1,720
Supplies & Expense	4,200	2,349
Travel	800	288
<u>Equipment</u>	<u>8,500</u>	<u>7,088</u>
Total Direct Costs	30,240	29,817
Total Indirect Costs	9,348	9,773
 Project Totals	 39,588	 39,590

Balance

<2>

Table 1. List of Results of HDN in Quinoline

No.	Catalyst		Reaction Conditions		Sulfided Temp. °C	Results K_D (l/hr)
	Composition	Support	Temp. °C	Pressure (psi)		
1)	HDS-9A					
2)	1.5% CoO-15% MoO ₃	γ -Al ₂ O ₃ (Harshaw)	350	700	400	0.24
3)	1.5% CoO-15% MoO ₃	AlCoaS-100 Al ₂ O ₃	350	700	400	0.11
4)	1.5% CoO-15% MoO ₃	η -Al ₂ O ₃	350	700	400	0.079
5)	1.5% CoO-15% MoO ₃	70% Al ₂ O ₃ -20% TiO ₂ -10% Cr ₂ O ₃	350	700	400	0.051
6)	1.5% CoO-15% MoO ₃	90% Al ₂ O ₃ -10% TiO ₂	350	700	400	0.070
7)	1.5% NiO-15% MoO ₃	70% Al ₂ O ₃ -20% TiO ₂ -10% Cr ₂ O ₃	350	700	400	0.055
8)	1.5% NiO-15% MoO ₃	70% Al ₂ O ₃ -20% TiO ₂ -10% Cr ₂ O ₃	350	700	400	0.06
9)	1.5% NiO-15% MoO ₃	70% Al ₂ O ₃ -20% TiO ₂ -10% Cr ₂ O ₃	350	700	400	The calcined time is 7 hrs longer than usual.
10)	1.5% NiO-15% MoO ₃	γ -Al ₂ O ₃ (Harshaw)	350	700	400	
11)	1.5% NiO-15% MoO ₃	η -Al ₂ O ₃	350	700	400	
12)	3.5% NiO-18% MoO ₃	γ -Al ₂ O ₃ (Harshaw)	350	700	400	CS ₂
13)	3.5% NiO-18% MoO ₃	γ -Al ₂ O ₃ (Harshaw)	350	700	400	
14)	3.5% NiO-18% MoO ₃	Cr ₂ O ₃	350	700	400	
15)	3.5% NiO-18% MoO ₃	TiO ₂	350	700	400	Calcined 2 hrs longer than usual
16)	3.5% NiO-18% MoO ₃	70% Al ₂ O ₃ -20% TiO ₂ -10% Cr ₂ O ₃	350	700	400	
17)	3.5% NiO-18% MoO ₃	70% Al ₂ O ₃ -20% TiO ₂ -10% Cr ₂ O ₃	350	700	350	
18)	3.5% NiO-18% MoO ₃	90% Al ₂ O ₃ -10% CrO ₂	350	700	400	

Table 2. List of Results of HDN in Decylamine

No.	Catalyst		Reaction Conditions		Sulfided Temp.	Results K_D (l/hr)
	Composition	Support	Temp. °C	Pressure (psi)		
1)	HDS-9A		350	700	400	0.68
2)	1.5% CoO-15% MoO ₃	γ -Al ₂ O ₃ (Harshaw)	350	700	400	1.0
3)	1.5% CoO-15% MoO ₃	AlCoaS-100 Al ₂ O ₃	350	700	400	1.2
4)	1.5% CoO-15% MoO ₃	90% Al ₂ O ₃ -10% ZrO ₂	350	700	400	0.93
5)	1.5% CoO-15% MoO ₃	ZrO ₂	350	700	400	0.59
6)	1.5% CoO-15% MoO ₃	TiO ₂	350	700	400	0.73
7)	1.5% CoO-15% MoO ₃	90% Al ₂ O ₃ -10% TiO ₂	350	700	400	1.8
8)	HDS-9A		350	700	400	0.22 added 16% wt. shale oil

Table 3. List of Testing Results in Shale Oil

No.	Catalyst		Reaction Conditions		Sulfided Temp.	Conversion at 10 Hrs.
	Composition	Support	Temp°C	Pressure (psi)		
1)	HDS-9A		350	700	400	10%
2)	HDS-9A		350	1000	400	8.4%
3)	HDS-9A		350	1400	400	18.6%
4)	1.5% CoO-15% MoO ₃	γ-Al ₂ O ₃ (Harshaw)	350	700	400	9%
5)	1.5% CoO-15% MoO ₃	TiO ₂	350	700	400	13%
6)	1.5% CoO-15% MoO ₃	ZrO ₂	350	700	400	12%
7)	1.5% CoO-15% MoO ₃	90% Al ₂ O ₃ -10% TiO ₂	350	700	400	10%
8)	1.5% CoO-15% MoC ₃	AlCat-10% Al ₂ O ₃	400	1000	400	32%





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DEPT OF CHEMICAL ENGINEERING J R KATZER ET AL.

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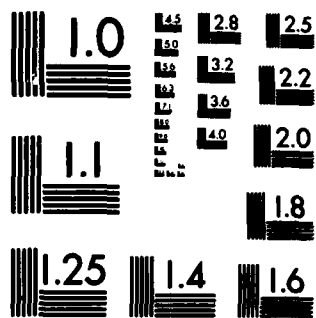
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SUPPLEMENTARY

INFORMATION



DEPARTMENT OF THE NAVY

NAVAL AIR SYSTEMS COMMAND
NAVAL AIR SYSTEMS COMMAND HEADQUARTERS
WASHINGTON DC 20361

IN REPLY REFER TO
NAVAIR-00D4

JUN 1 1983

AD-A111559

From: Commander, Naval Air Systems Command, Code (AIR-00D4) Washington, D. C. 20361
To: Administrator
Defense Technical Information Center for
Scientific and Technical Information
Cameron Station, Building #5
Alexandria, Virginia 22314

Subj: Technical Report University of Delaware; change of contract number, AD A111 559

1. The subject report was forwarded to your office, 26 February 1982, under an erroneous Contract Number N00019-80-K-0507.
2. It is requested that the contract number be changed to N00019-81-C-0153.

Pat Stone
Pat Stone
by direction

